# MATERIALS SCIENCE

## Packing and the structural transformations in liquid and amorphous oxides from ambient to extreme conditions

*Liquids and glasses diffractometer D4*

Network-forming structural motifs such as $SiO_4$ tetrahedra play a key role in governing the physical and chemical properties of disordered oxide materials, which range from photonic glasses to the fluids in planetary interiors. Here we show that the coordination number of these motifs, which has a profound effect on the connectivity of an atomic network [1], can be rationalised in terms of the oxygen-packing fraction over an extensive pressure and temperature range.

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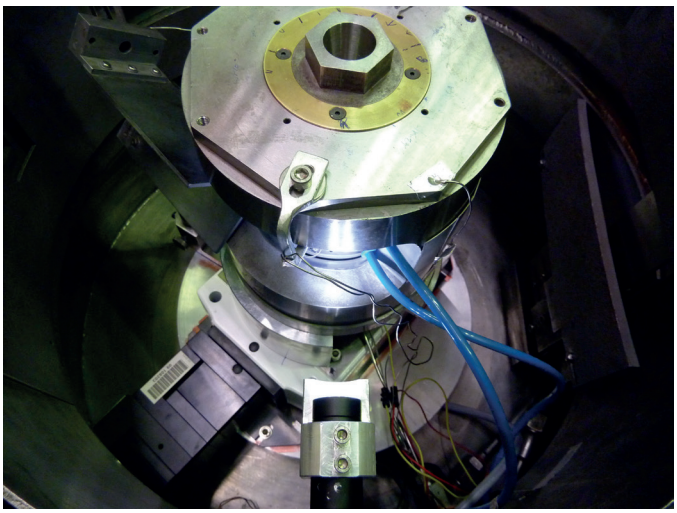
At ambient conditions in a material such as silica glass (the main component of optical fibres), an open network is formed from corner-linked $SiO_4$ tetrahedra. When the glass is compressed the network collapses, and a point is reached where the Si-O coordination number (meaning the average number of oxygen O atoms around an Si atom) increases: $SiO_4$ tetrahedra transform into corner- and edge-linked $SiO_6$ octahedra. These changes affect the network connectivity and hence the physico-chemical properties of the material. But is there a way of predicting when such changes must occur, and can this be generalised to other oxide materials under extreme conditions **(figure 1)**?

To help answer these questions, information is required on the A-O coordination number $\bar{n}_A^O$ for network-forming structural motifs such as $AO_3$ triangular units and $AO_4$ tetrahedra, where A denotes a chemical species such as B, Si or Ge. These coordination numbers can be measured under extreme conditions by using neutron or X-ray diffraction. After consulting the available literature, we performed complementary diffraction experiments. For instance, the neutron diffractometer D4 at the ILL was used to measure the structure of glassy $B_2O_3$, $SiO_2$ and $GeO_2$ using a Paris-Edinburgh press at pressures up to 8.5 GPa **(figure 2)**. These experiments took advantage of

**Figure 1**
An illustration of liquid oxides under extreme conditions.

**Figure 2**
A Paris-Edinburgh high-pressure press mounted on the diffractometer D4 at the ILL.



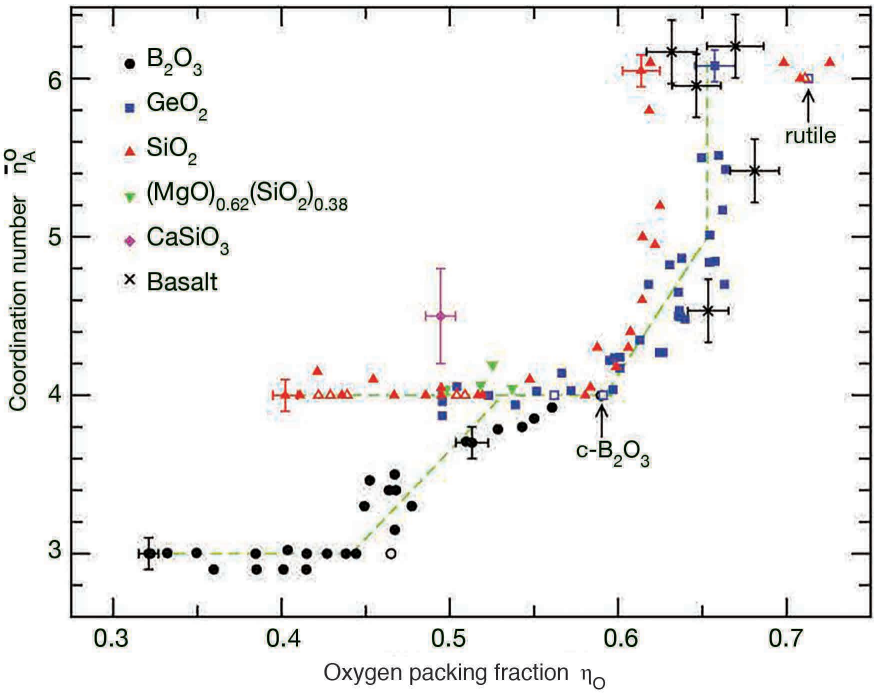



**Figure 3**

The dependence of the A-O coordination number $\bar{n}^O_A$ for A-centred (A = B, Ge or Si) network-forming structural motifs on the oxygen-packing fraction $\eta_o$ for a variety of glassy and liquid oxide materials under extreme conditions [3]. Results are given for glassy $B_2O_3$, $SiO_2$, $GeO_2$ and $(MgO)_{0.62}(SiO_2)_{0.38}$ under pressure; liquid $CaSiO_3$ at high pressure and high temperature; and molten basalt under deep mantle conditions. The open symbols correspond to the room-temperature polymorphs of crystalline $B_2O_3$, $SiO_2$ and $GeO_2$.

developments made under the aegis of an ILL long-term proposal (LTP-6-1, [2]). For example, the combination of a short incident neutron wavelength of 0.5 Å and excellent counting statistics, coupled with a low and stable background, ensured the measurement of reliable A-O coordination numbers.

If the $\bar{n}^O_A$ values measured at different pressures and temperatures are plotted against the oxygen-packing fraction $\eta_o$, namely the fraction of volume in a glass or liquid that is occupied by oxygen atoms, then a structural map emerges **(figure 3)** [3]. This map gives a means for predicting the likely regimes of topological change. For example, the $SiO_4$ tetrahedra that are present in silica glass under ambient conditions start to become unstable as the density increases and the oxygen-packing fraction approaches the range $\eta_o$ = 0.55–0.60 expected for a random loose packing of hard spheres. With further increase of density, the Si-O coordination number continues to grow so that $SiO_6$ octahedra predominate as the oxygen-packing fraction approaches the limit $\eta_o$ = 0.64 expected for a random close packing of hard spheres [4].

The structural map will prove useful in helping to predict the network connectivity of a given material under high-pressure and high-temperature conditions, and when this connectivity is likely to change. Such information is important for understanding the properties of magma-related melts because the topology of a network will affect its compressibility and transport properties such as the viscosity. Information on the network connectivity is also pertinent for understanding the properties of high-density liquids to aid in the design of new glasses with the desired structural and functional properties **(figure 4)** [5].

**Figure 4**

The structure and properties of liquid and amorphous oxide materials can be manipulated by modifying the network connectivity via control of the packing fraction of spherical oxide ions.